A Single Active Site Metal Center of Neodymocene Chloride for the Ring-Opening Polymerization of ε-Caprolactone

Weifeng Hou, Jin Chen, Xiaoli Yan, Zuyun Shi, Junquan Sun

Department of Chemical Engineering, Zhejiang University, Hangzhou 310027, China

ABSTRACT: A germyl-bridged lanthanocene chloride, $Me_2Ge(^tBu-C_5H_3)_2LnCl$ (Ln = Nd; (Cat-**Nd**), was prepared and successfully used as single catalyst to initiate the ring-opening polymerization of ε-caprolactone (ε-CL) for the first time. Under mild conditions (60°C, [ε-CL]/[Ln] = 200, 4 h), Cat-**Nd** efficiently catalyzes the polymerization of ε-CL, giving poly(ε-caprolactone) (PCL) with high molecular weight (MW) ($>2.5 \times 10^4$) in high yield ($>95\%$). The effects of molar ratio of [ε-CL]/Cat-Nd, polymerization temperature and time, as well as solvent were determined in detail. When the polymerization is carried out in bulk or in petroleum ether, it gives PCL with higher MW and perfect conversion (100%). The higher catalytic activity of this neodymocene chloride could be ascribed to the bigger atom in the bridge of bridged ring ligands. Some activators, such as $NaBPh_4$, KBH_4, $AlEt_3$, and $Al(i-Bu)_3$, can promote the polymerization of ε-CL by Cat-**Nd**, which leads to an increase both in the polymerization conversion and in the MW of PCL. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 1212–1217, 2012

Key words: ring-opening polymerization; ε-caprolactone; germyl-bridged lanthanocene chloride; poly-ε-caprolactone

INTRODUCTION

Ring-opening polymerization of ε-caprolactone (ε-CL) provides a convenient way for preparing poly-ε-caprolactone (PCL),[1–4] which may be used as synthetic biomaterial or controlled drug release matrix. Therefore, much attention has been paid to the study of catalysts for ring-opening polymerization of ε-CL. Various alkoxides or carboxylates containing tin,[5–7] germanium,[8] aluminum,[9] alkali,[10] zinc,[11] or early transition metals[12,13] have been developed for the ring-opening polymerization of ε-CL.

For the last two decades, rare earth metal compounds have been explored as a further efficient initiator of the ring-opening polymerization of ε-CL. Lanthanide alkoxides were reported by Mclain, Drysdale[14] and Shen et al.[15–18] to be active catalysts to initiating ε-CL polymerization with high conversion (up to 100%). The catalytic activity of rare earth halides can be increased greatly by addition of epoxide ([$NdCl_3$] = 3.0×10^{-3} mol/L, Propylene Oxide/$NdCl_3$ = 20, 30°C, 4 h, conversion = 100%, M_w = 2.21

$\times 10^5$).[19] Rare earth phenyl derivatives compound, 2,6-dialkoxylphenyl lanthanoide complexes[20] or 2-methyphenyl samarium,[21] can initiate the polymerization of ε-CL with high activities. Rare earth compounds with Ln-N bonds ({[$(MeC_5H_4)_2Ln[O=C=N(CH_2)_4CH_2]$]$_2$(Ln = Yb,Y,Er)[22];$(Siam)_3Ln$,$(C_5Me_5CMe_2)_2Ln(Siam)$(Siam = $PhC(NSiMe_3)_2$)[23]) have also been found to be very active in initiation of the ring-opening polymerization of ε-CL. Lanthanocene complexes which possess well-defined structures and living polymerization characteristics have also attracted much attention. Yasuda,[24] Novak[25] and Shen[26] reported their elegant research on the living ring-opening polymerization of ε-CL with trivalent organolanthanides, such as $SmMe(C_5Me_5)_2(THF)$ ([ε-CL]/[Sm] = 500, 25°C, 5 h, conversion = 95%, M_n = 8.34×10^4, M_w/M_n = 1.06), and other complexes [$SmH(C_5Me_5)_2$]$_2$,and [($^tBuCp)_2NdCH_3$]$_2$ for ε-CL polymerization. Evans et al.[27,28] have reported that $(C_9H_7)_2Sm(THF)_x$ and $(C_{13}H_9)_2Sm(THF)_2$ showed much higher activities than $(C_5Me_5)_2Sm(THF)_x$ in ε-CL polymerization in THF, which may be caused by the former two complexes having more open coordination environments around the metals. Most of the rare earth compounds described above have σ-bonds of the type Ln—O, Ln—C, Ln—H, Ln—N, and Ln—B recently reported,[29–32] which may play the key role in initiation of ε-CL polymerization. However, there is no example of germyl bridged rare earth metallocene halides in literature for the polymerization of ε-CL.

TABLE I
Bulk Ring Opening Polymerization of ε-CL by Various Rare Earth Metal Compounds

No.	Catalyst	[ε-CL]/[Ln]	t (h)	T (°C)	M_η (×10^4)	Conversion (%)
1	Me$_2$Ge(^{t}BuC$_5$H$_3$)$_2$NdCl	200	4	60	2.74	100
2	(Cat-**Nd**)	120	40	100	4.5	82.5
3	YCl$_3$	120	40	100	4.7	85.0
4	NdCl$_3$	200	4	60	7.9	48
5	O(C$_2$H$_4$C$_5$H$_3$Me)$_2$YCl (Catalyst 3) Me$_2$Si(Me$_3$SiC$_5$H$_3$)$_2$NdCl (Catalyst 4)	200	5	70	18.4	100

No.: 2,3: Refs. [15–18]; 4,5: Ref [33].

During the last decade, we have reported that both O(C$_2$H$_4$C$_5$H$_3$Me)$_2$YCl and Me$_2$Si(Me$_3$SiC$_5$H$_3$)$_2$NdCl are active in initiation of ε-CL polymerization, producing high molecular weight (M_w) PCL in a bulk system[33] (see Table I). As known, carbon and silicon are often used in the bridge of the metallocene bearing bridged cyclopentandienyl ligands. The radius of germanium is larger than them of above (atomic radius, pm^{-1}: C, 77; Si, 118; Ge, 123.[34]), which might be reasonable anticipantated germyl bridged metallocene having more open coordination environment. It could be favorable for monomer coordination and insertion in polymerization process. On the basis of our previous research, herein we report another germyl-bridged neodymocene chloride, Me$_2$Ge(^{t}BuC$_5$H$_3$)$_2$LnCl [Ln = Nd(Cat-Nd), in the initiation of the ring-opening polymerization of ε-CL, exhibiting satisfying catalytic behaviors.

EXPERIMENTAL

Materials

ε-CL (Mitsubishi) was dried and distilled over CaH$_2$ under reduced pressure and then stored in a refrigerator. Toluene, petroleum ether, and tetrahydrofuran (THF) were distilled over blue benzophenone-Na complex. CH$_2$Cl$_2$ was dried over CaH$_2$ and distilled prior to use.

Measurements

The intrinsic viscosity [η] of PCL was determined in DME at 30°C with an Ubbelohde viscometer. The viscosity-average molecular weight (M_η) was calculated by the following equation[35]: [η] = 1.91 × 10^{-4} $M_\eta^{0.73}$. The molecular weight distribution (MWD) of PCL were recorded using a gel permeation chromatograph (Water-Associates M730) in THF at 25°C with polystyrene as the standard. IR spectra were recorded on a Nicolet E.S.P. 560 FTIR apparatus. Mass spectra were recorded with ESI on an Esquire-LC spectrometer. GC/MS spectra were recorded on an HP 6890/5973 spectrometer; recorded at EI, T =

50–270°C, EM = 70 eV. ^{1}H NMR spectra were obtained on a Bruker AC-200 spectrometer in CDCl$_3$. Elemental analysis was conducted on a Perkin–Elmer 240 elemental analyzer.

Preparation of novel complexes Me$_2$Ge(^{t}BuC$_5$H$_3$)$_2$LnCl$_2$Li(THF)$_3$ (Ln = Nd)

The ligand, Me$_2$Ge(^{t}BuC$_5$H$_4$)$_2$, was prepared according to the procedures for similar compounds.[36,37] ^{1}H NMR (200 MHz, CDCl$_3$): δ 5.8–6.7 (m, 6H, CpH), 2.15 (m, 2H, CpH), 1.18 (s, 18H, CMe$_3$), −0.11 (s, 6H, GeMe$_2$). GC/MS(EI): 97.3%, m/z 346 (5.2, M$^+$), 225 (100, MeGe(^{t}BuC$_5$H$_4$)$^+$), 169 (54.2, Me$_2$Ge(C$_5$H$_5$)$^+$), 139 (12.5, C$_5$H$_5$Ge$^+$).

In analogy to the procedure in references,[36,37] a 100-mL Schlenk flask with a magnetic stirring bar was charged with 0.80 g (2.3 mmol) Me$_2$Ge(^{t}BuC$_5$H$_4$)$_2$ dissolved in 30 mL THF. The solution was cooled to 0°C and 2.1 mL (4.6 mmol) of n-BuLi (2.18 mol/L in petroleum ether) was syringed into it. The solution turned into orange and was stirred for 12 h at room temperature. A turbid mixture of 30 mL THF and 0.59 g (2.3 mmol) of NdCl$_3$ was stirred in another 100-mL flask for 24 h, and then added to the above solution. The mixture turned into a clear blue solution and was stirred for an additional 24 h at room temperature. The solvent was then removed and the resulting greenish-blue residue was extracted three times with CH$_2$Cl$_2$ (3 × 15 mL). 0.63 g of blue crystals (35.1% yield) was obtained by decanting the solvent. MS (ESI): m/z 780 (100, M$^+$), 781 (68, M$^+$+H), 782 (M$^+$+2H), IR (cm^{-1}): 650s, 813s, 915s, 982w, 2904s, 3050w. Anal. Calcd for C$_{32}$H$_{54}$O$_3$Cl$_2$LiNdGe: C, 49.18%; H, 6.96%; Found: C, 49.09; H, 7.04.

Polymerization

All polymerizations were carried out in a 25-mL ampoule, which was heated in an oven, evacuated, and filled with pure argon for several cycles before use. Catalyst, ε-CL and solvent were introduced into an ampoule sequentially. The ampoule was then placed
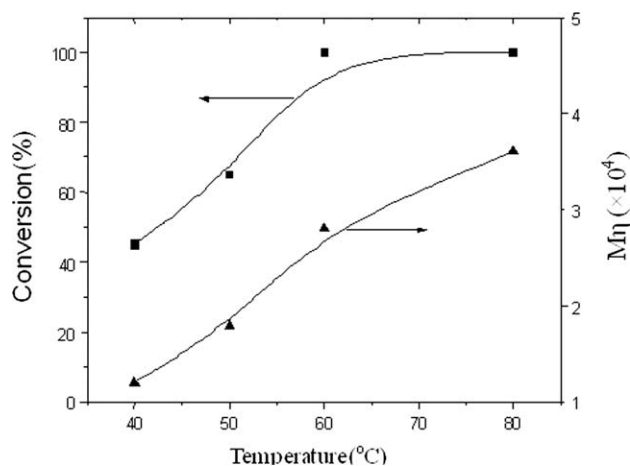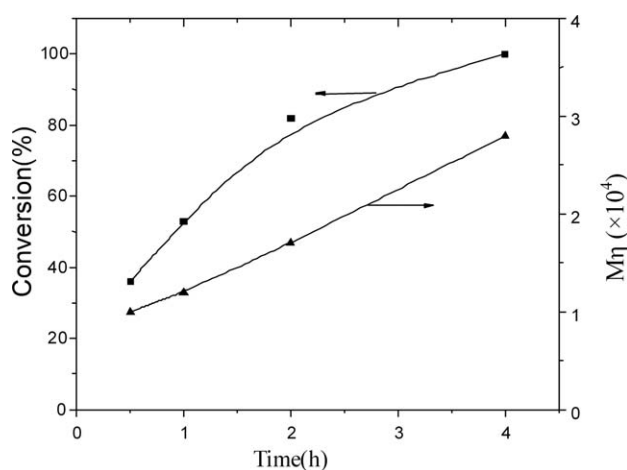
Figure 1 Cat-**Nd** effect of polymerization temperature Polymerization conditions: 4 h, [ε-CL]/[Nd] = 200, ε-CL 0.5 mL, bulk polymerization.

in a water bath or an oil bath kept at constant temperature. Afterwards, the polymer was precipitated in excess ethanol (containing 5% HCl) and washed with fresh ethanol for several times, and then dried at 50°C under vacuum.

RESULTS AND DISCUSSIONS

Bulk polymerization of ε-CL

As shown in Table I, although rare earth halides were found to catalyze the polymerization of ε-CL at high temperature, the catalytic activities were very low because of the stability of the Ln-Cl bond.[19] However, when two of the three chlorine atoms of LnCl$_3$ are substituted by two cyclopentadienyl rings, the bridged lanthanocene chlorides showed unique catalytic properties in the polymerization of ε-CL producing PCL with high molecular weight in good

Figure 2 Cat-**Nd** effect of the polymerization time polymerization conditions: 60°C, [ε-CL]/[Nd] = 200, ε-CL 0.5 mL, bulk polymerization.
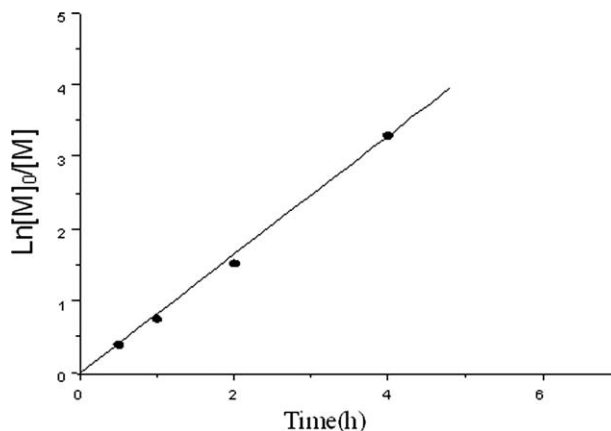
Figure 3 ln[M]$_0$/[M] versus t for Cat-**Nd.**

yield.[33] From Table I, it can also be seen that, under the same conditions, the catalytic activities of lanthanocene chlorides containing a mono-atomic bridge of germanium are obviously higher than that of ether bridged yttrocene chloride, which might be attributed to bigger germanium mono-atom bridged lanthanocene chloride having a more open coordination environment around the metal for monomers. The greater opening of the metal coordination sphere in the vicinity of the σ-ligand result in the insertion of ε-caprolactone into the σ bonds relatively easier.[31]

From Table I it can be found roughly that the catalytic activities of both chloride salt and lanthanocene of Nd are somewhat higher than them of Y corresponding compounds, which is accordance with the results reported by Yasuda.[38] Namely larger metal atom is favorable to increasing catalytic activity (atomic radius, pm^{-1}: Nd, 181; Y, 178[34]). (As also known, ionic radius: Nd^{3+} > Y^{3+}.)

The results of bulk polymerization of ε-CL with Cat-Nd are presented in Figures 1–4. The polymerizations proceeded so fast that almost 100% polymerization conversion and a PCL with molecular weight of about 3 × 10^4 could be obtained usually within 4 h at 60°C.

The effect of temperature on polymerization

As illustrated in Figure 1, both the conversion of monomer and the molecular weight of the PCL increase with rising polymerization temperature (from 40 to 80°C). This may be attributed to the intensive activation of monomer molecules at higher temperatures. On the other hand, the founding indicates that the active species are still stable even at 80°C. The thermal stability of germyl-bridged metallocenes have also been confirmed in the polymerization of ethylene.[37] The GPC result in Figure 5 shows the molecular weight distribution (MWD = 1.34) of PCL produced by Cat-Nd at 80°C. Obviously there
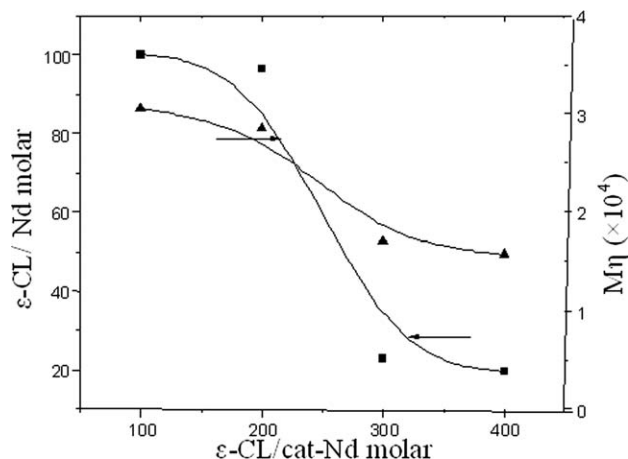
Figure 4 Cat-**Nd** Effect of [Cl]/[Nd] molar ratio with polymerization conditions: 60°C, 10 h, ε-CL 0.5 mL, bulk polymerization.

are not violent side reactions, such as chain termination and transesterification occurring at higher temperatures. This may be again attributed to the intensive activation of monomer molecules at higher temperatures.

The effect of time on polymerization

The influence of polymerization time on the conversion of ε-CL and the molecular weight of PCL is plotted in Figure 2. The linear relationship of $\ln([M]_0/[M])$ and t in Figure 3 indicates that the increase in yield follows first order kinetics up to about 4 h. This is in good agreement with the result ε-CL polymerization in a previous report.[39]

The effect of the molar ratio of [ε-CL]/[Nd] on polymerization

Figure 4 indicates that at low [ε-CL]/[Nd] molar ratio, ε-CL can completely convert into PCL, but the
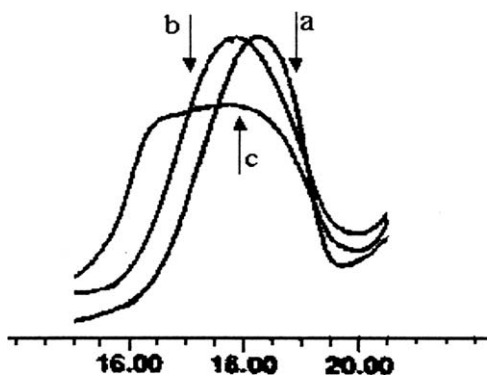
Figure 5 GPC curves of PCL prepared by Cat-Nd polymerization conditions: [CL/Nd] = 200, 60°C, 2 h, bulk (a) no Lewis base, M_w/M_n = 1'34; (b) AlEt$_3$/Cat = 15, M_w/M_n = 1.43; (c) NaBPh$_4$/Cat = 1, M_w/M_n = 1.83.

TABLE II
Bulk Polymerization of ε-CL Catalyzed by Cat-Nd in the Presence of Activators

No.	Cocatalyst	[Cocatalyst]/[Cat-Nd]	M_η ($\times 10^4$)	Conversion (%)
1	NaBPh$_4$	0	1.62	79.4
2	NaBPh$_4$	1	2.35	92.3
3	NaBPh$_4$	2	2.27	89.9
4	KBH$_4$	2	2.01	87.6
5	AlEt$_3$	10	1.87	100
6	AlEt$_3$	15	2.15	100
7	AlEt$_3$	20	1.97	91.5
8	Al(i-Bu)$_3$	15	1.85	92.7

Polymerization conditions: 60°C, 2 h, [ε-CL]/[Nd] = 200, ε-CL 0.5 mL.

conversion of ε-CL drops rapidly on further increase of the [ε-CL]/[Nd] molar ratio. The molecular weight of PCL at first changes only a little and then decreases rapidly when the [ε-CL]/[Ln] molar ratio exceeds 200, which might be caused by some side-reaction, such as coordinative competition between active polymer chain and monomer, transesterification,[18,39] or chain termination by impurities in ε-CL.

The effect of activators on the polymerization

As is known, most Group IV metallocene chloride catalysts can be activated by some cocatalysts like B(C$_6$F$_5$)$_3$, Ph$_3$CB(C$_6$F$_5$)$_4$, or MAO to form very active cationic species, which are isoelectronic to neutral lanthanocenes.[40–42] As mentioned above, lanthanocene hydride or alkyl compounds are extremely active for the polymerization of ε-CL. However, germyl-bridged lanthanocene chlorides should belong to the precursors of their corresponding hydride or alkylate compounds. Hence, in this study, NaBPh$_4$, KBH$_4$ and trialkyl aluminum such as AlEt$_3$, Al(i-Bu)$_3$ were used to test the promoting effect on the polymerization of ε-CL by Cat-Nd. The results are summarized in Table II. All these additives were found to promote the polymerization of ε-CL.

As shown in Figure 5, the profile of the GPC curve shows only one peak in the chromatogram of PCL produced by the single component catalyst, meanwhile, although the molecular weight distribution of

TABLE III
Effect of Solvent on the Polymerization of ε-CL Catalyzed by Cat-Nd

Solvent	ε	Conversion (%)	M_η ($\times 10^4$)
Petroleum ether	/	100	2.53
Toluene	2.33	94.6	2.07
Tetrahydrofuran	7.85	56.2	1.52
Dichloromethane	10.45	34.4	1.07

Polymerization conditions: 60°C, 1 h, [ε-CL]/[Nd] = 100, ε-CL 0.5 mL, solvent 0.5 mL.

PCL obtained by the binary catalyst system becomes broader, there are no obvious double peaks in GPC chromatogram, and so it can be proposed that in the binary catalyst system there might be only one new active species produced by the combination of Cat-Nd with the corresponding cocatalyst.

The effect of solvent on the polymerization

To determine the effect of the solvent medium on the polymerization of ε-CL, several solvents with different dielectric constants (ε) were used in the polymerization. Table III indicates that in nonpolar solvent such as petroleum ether, ε-CL is polymerized almost completely within 1 h at 60°C, and the molecular weight reaches 2.53×10^4 which is similar to bulk polymerization due to the precipitation of PCL in petroleum ether. Under the same condition, a conversion of 94.6% and PCL with MW 2.07×10^4 were obtained in toluene. However, in polar solvents, such as THF and CH_2Cl_2, the yields were only about 50% or less. Moreover, the molecular weights of PCL obtained from THF or CH_2Cl_2 were much lower than those from toluene or petroleum ether, which is probably due to the competition of the polar solvent molecules in coordination with active catalytic species, thereby hindering the further coordination of monomer molecules.

Polymerization mechanism

The interest of the new single catalyst for polymerization is not only in the exploration a new catalyst but also in the study of polymerization mechanism. The single catalyst in general has well-defined composition and/or structure, which is different from typical Ziegler-Natta catalyst.

The present polymerization mechanism could be postulated to be the coordination insertion in two manners (indicated above) as similar polymerization reports in literatures,[19,38] which must be proved by the ^{1}H NMR analysis of the resulted oligomer, but at present it is difficult to identify the coordination way from the signals of the determined spectra. It might be arisen from to the complex to be too sensi-
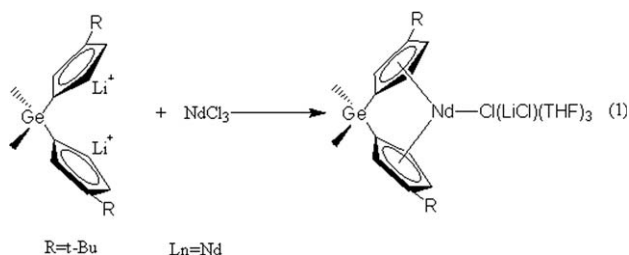
Scheme 1 Cat-Nd synthesis route.
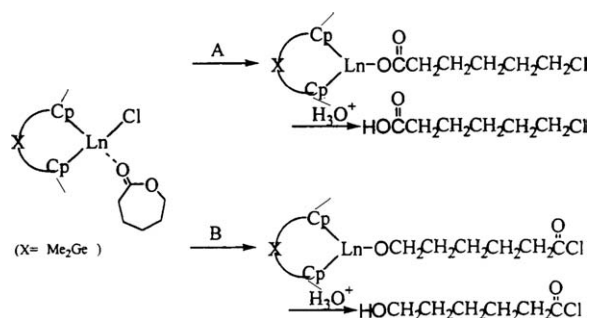
Scheme 2 Postulated polymerization process.

tive to moisture and other impurities. However, this research should be performed in detail in future. Furthermore, from the similarity of monomers, it is notable to test the ring-opening polymerization of other monomers, such as valerolactone, butyrolactone, lactide, and others by the present neodymocene chloride complex and study the polymerization mechanism, if it is possible.

CONCLUSIONS

A germyl-bridged neodymocene chloride, $Me_2Ge(^{t}BuC_5H_3)_2NdCl$, has been synthesized and used as an active single catalyst for the ring-opening polymerization of ε-caprolactone, providing high molecular weight poly(ε-caprolactone) in high yield. Higher temperatures favor catalytic activities. In the bulk or in petroleum ether, ε-caprolactone can be polymerized completely. Activators such as $NaBPh_4$, KBH_4, $AlEt_3$, and $Al(i-Bu)_3$, can promote the polymerization of ε-caprolactone to produce high molecular weight PCL with relatively narrow MWD.

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